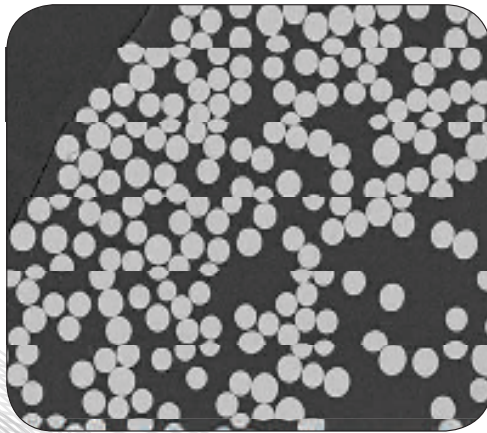


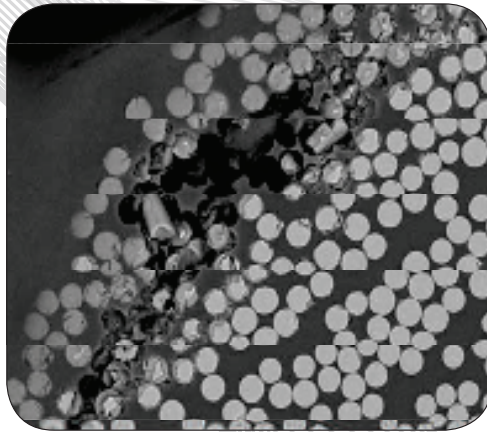


INNOVATIONS FOR LIVING®

AN INSIDE LOOK AT **CORROSION** IN **COMPOSITE LAMINATES**



Advantex® Glass



E-Glass

Boron-Free E-CR Glass Fibers Demonstrate Superior Corrosion Resistance Compared to E-Glass When Used in Composite Structures Exposed to Sulfuric Acid. Previous Research on Leaching Mechanism of E-Glass in Acids is Confirmed Visually.

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April 2010

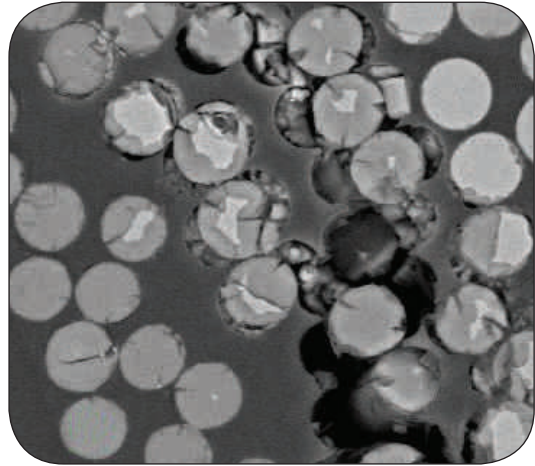


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Abstract

The superior corrosion performance of boron-free Advantex® E-CR glass compared to E-glass has been shown in many ways.

Numerous bare-glass corrosion studies have compared various glass compositions but do not necessarily reflect composite corrosion performance. ASTM C581 composite corrosion performance testing shows composite performance in a “no-stress” testing methodology and thus is really a resin test rather than a test of a composite system under load. Stress-corrosion work started by Mark Greenwood at Owens Corning in the mid-1990s and continued at the company tests composites under load and provides a compelling reason for using superior glass reinforcement (Advantex® E-CR glass) throughout the structure. The mechanism for the corrosion of E-glass has been inferred through previous leaching studies. This paper shows E-glass deterioration visually and the mechanism by which it occurs.



Introduction

There are a number of ways in which the corrosion of E-glass has been studied relative to other glass fiber products. A comparison of bare-glass corrosion in various corrosive media is the simplest. But it is an incomplete way of understanding what happens in the

““ *The focus of this paper is to show the mechanism by which corrosion occurs over time in stressed laminates.* ””

composite part. A comparison of glass fibers in ASTM C-581 coupons can show differences between E-glass and Advantex® E-CR glass, but the test was originally designed to compare the performance of

corrosion resistant resins in a no-load condition. Any differences between E and E-CR glass in an ASTM C-581 must be very large to show a difference. Mark Greenwood’s stress-corrosion work started in the mid-1990s and continued today by Kevin Spoo combines both corrosion and stress to predict the relative performance of E-glass compared to Advantex® glass under these dual conditions. The focus of this paper is to show the mechanism by which corrosion occurs over time in stressed laminates using SEM (Scanning Electron Microscopy) and EDX (Energy Dispersive X-ray) spectrometry.



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Corrosion of Glass Fibers

Most composite materials intended for corrosion resistant applications are designed to protect the structural fibers within the architecture of the part. This paper is not going to delve into that, but instead focus on what happens as corrosive materials gain access to the structural portion of a laminate.

What we think happens, and numerous publications support this view, is that corrosive materials gain access to glass fibers through the protective coatings or resin matrix. Quality coatings or resin matrices can slow corrosion by addressing the several mechanisms by which corrosive materials gain access to the glass fibers. These mechanisms include access through cracks in the resin matrix created as a result of: 1) matrix shrinkage, 2) applied stress or strain as part of the design, 3) environmental cycling (which is really a stress or strain), or 4) damage through impact (which is another stress or strain).

“Corrosive materials gain access to glass fibers through the protective coatings or resin matrix.”

Other mechanisms which do not rely on cracks are: 5) process upset exposing resin matrix to more corrosive materials than were intended, 6) poor resin matrix selection and 7) diffusion of the corrosive material through the intact resin matrix. The effect of diffusion is highly dependent on the corrosive media and the resin matrix. Previous studies have gathered data to quantify the effect of corrosion on the glass fibers. In this study, we attempt to actually see (visually) the corrosion progress over time.

Testing Process

This study focused on the corrosion of glass fiber-reinforced composite rods that were exposed to a ~1% strain for a brief period of time and then immersed in a 10% sulfuric acid solution under no-load and room temperature for an extended period of time. After regular intervals the rods were removed and examined for the effects of corrosion.

This experiment used 17u E-glass and Advantex® glass fibers with the same identical sizing system and resin system to make pultruded rods. In order to ensure that the strain induced in the production of the rods was minimized, the glass fibers for making the rods were pulled by hand and not using a pultrusion machine.

Skins of glass fiber were weighed, pulled through a resin bath and into hollow glass rods. The rods were then cured in an oven to ensure full and complete cure of the resin system. The resin system in this case was an isophthalic-acid-based unsaturated polyester resin at 400cps initiated with 1% BPO pre-dissolved in styrene.

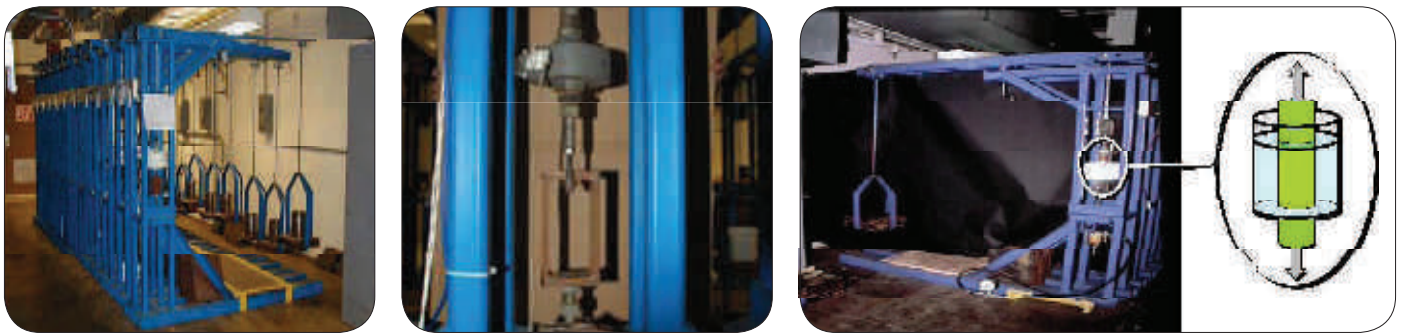
After curing, the glass tubes were lightly rapped to shatter them and the hand-pulled pultruded rods were removed. Tabs consisting of steel tubing were bonded to the sanded rod ends using epoxy resin. The tabbed rods were placed in an Instron® tester and the breaking strength of the rods determined. A cantilever beam frame (see photos below) was then loaded with a load cell in place such that a 1% strain would be induced in the rod when placed in the fixture. The frame was unloaded, the load cell removed, the rod placed in the frame and the rod loaded to 1% strain. The rod remained in place for 72 hours.



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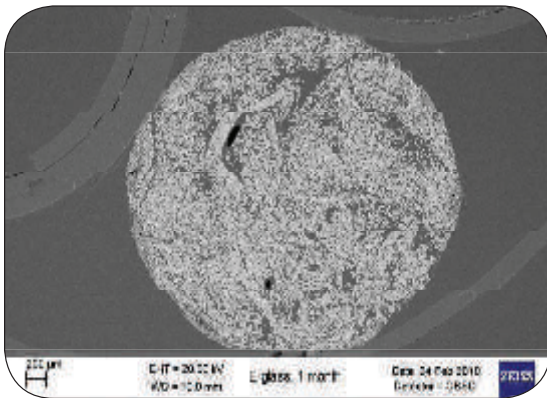
When the rod was removed, it was cut into 2" long pieces and immersed in a 10% sulfuric acid solution. It remained in this solution at 25°C for several months. Rod pieces were removed periodically and examined by the Owens Corning Microscopy Lab. Unlike the photo on the far right shown below, these rods were not exposed to corrosive fluid under stress as is typical in stress-corrosion testing.

The preparation procedure used in the Microscopy Lab was to pot the sample in epoxy resin and remove about 1 mm of material from the rod end through polishing of the sample. SEM photos were taken of the rod cross-sections at various levels of magnification. Additionally, when corrosion of fibers was seen, EDX spectrographs were made to determine if corrosion was actually taking place by monitoring compositional changes in areas of the glass fiber.

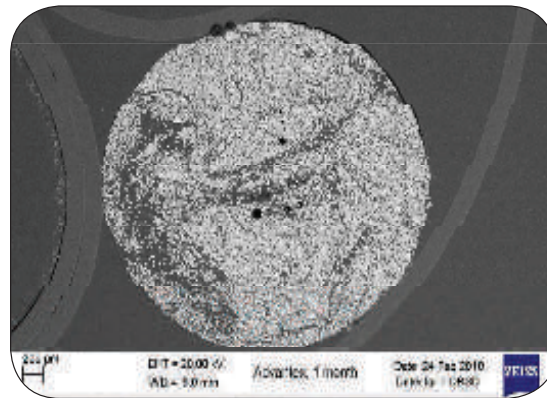


Findings and Discussion

The SEM photos below were taken in back-scatter mode. An interesting feature of SEM is that electrons scattered from the surface of the part being examined will reflect a greater number of electrons from harder surfaces, such as solid glass fibers. Softer or porous surfaces like resin will reflect fewer electrons and voids reflect nothing. In SEM photographs, solid glass appears white or light gray, porous glass appears gray, resin appears dark gray and voids are black.



1. E-glass rod, one month in 10% H₂SO₄



2. Advantex® glass rod, one month in 10% H₂SO₄

Photos 1 and 2 show low magnification views of the E-glass and Advantex® glass samples after one month exposure to 10% sulfuric acid. The photos serve as a reference of the corrosion resistance of each glass type before examining selected areas of the rods. They also serve as a reference when comparing the differences between one-month exposure and three-month exposure.

When looking at the 1/8" E-glass rod in cross-section (photo 3), what we see is white fibers near the center of the rod, gray fibers at the exterior of the rod and voids apparent along the crack. The gray fibers have had components of the glass leached from the fiber. This proceeds from the outside of the rod inward and from the outside of the individual filaments inward.

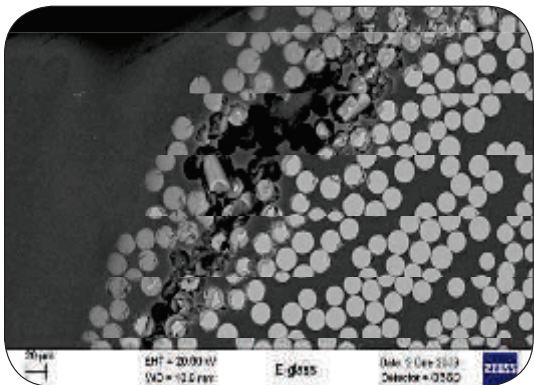
A de-bonding of a number of fibers from the resin matrix has also occurred. The task of polishing the surface to obtain these photomicrographs could be suspected of creating these cracks, but normally if that had occurred cracks would be dispersed throughout the circumference of the part, and they are not. The rods were under no stress during chemical exposure, so a likely cause could be latent resin shrinkage as the resin de-bonds from the fiber and the fiber disappears.

“Confirmation of leaching was obtained by running EDX spectrometry on fibers”

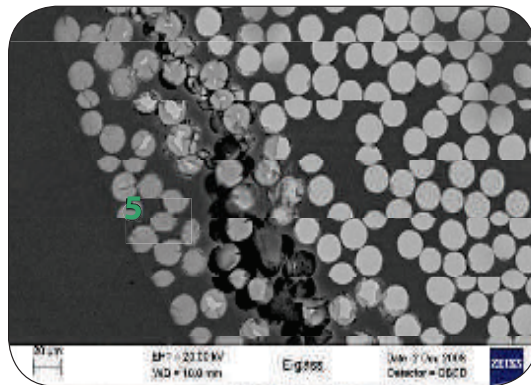
This resin, like most unsaturated polyesters, has an 8% volumetric shrinkage and latent built-up stress is possible. The task of polishing accounts for some of the fibers being pulled out of what is now a void area. The empty holes where fibers were previously, appears black (void).

Confirmation of leaching was obtained by running EDX spectrometry on fibers in photos 4 and 5 with the locations of each sampling appearing with green numbers on the sampling locations. EDX is a fast and convenient tool for measuring the composition of glass fibers but it does have some drawbacks. It cannot measure elements of atomic weight lower than carbon (C), and this includes boron (B). Boron is a key element in E-glass and previous studies have shown it is attacked readily by acids.

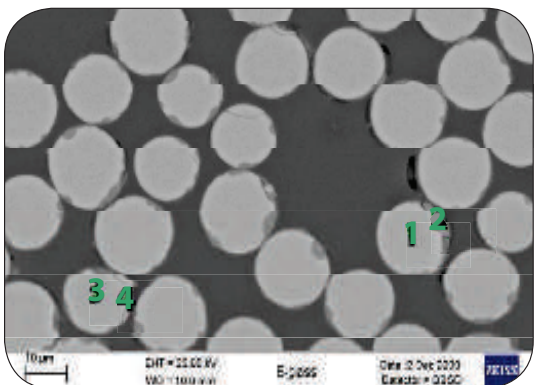
In fact, previous studies have shown the presence of boron dramatically increases the leaching rate of E-glass until only a silicate structure is left. An internal study at Owens Corning in 1986 identified boron as the ingredient that caused glass to leach at a faster rate than similar glasses made without boron. A more recent published study concluded that boron is the keystone that allows the leaching of other metal oxides in the glass.¹



3. E-glass rod, one month in 10% H₂SO₄



4. E-glass rod, one month in 10% H₂SO₄



5. E-glass rod, one month in 10% H₂SO₄

¹Advanced Materials Research, Vols. 39 and 40, April 2008, pp 311-316, by Robert Jones, Department of Applied Chemistry, Curtin University, Perth Australia



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The sampling locations in photos 4 and 5, and subsequent photos (green numbers), are referenced on the top of Table 1. The composition of this E-glass fiber is known and is shown in column zero in the table below.

An EDX analysis of the fiber that has not yet been corroded is shown in columns 1 and 3 while columns 2, 4, and 5 (highlighted in gray) show the analysis of fibers that have gray patches (shown in the photos) indicating corrosion. The EDX analysis of columns 1 and 3 compared to that of column zero shows the shift in percentages of various oxides of each element of the glass fiber that occurs as a result of the limitations of the EDX.

The inability to measure boron, which typically represents 5 to 6% of an E-glass formulation, could easily account for the numerical shift seen from column 0 to columns 1 and 3. This establishes a baseline of comparison. Greenwood¹ and Hofmann² have shown boron to be one of the elements to be leached rapidly from glass fibers exposed to acid but the EDX cannot confirm this directly due to limitations of using this method. But, it can be inferred indirectly by the rise in silica percentages in corroded areas. The previously referenced works (¹ and ²) measured elements leached from the glass fibers in 5% or 10% hydrochloric acid solutions using ICP (Inductively Coupled Plasma) spectrometry. In these studies, the elements with the highest leach rate are similar to the depletion of similar elements (represented as the oxide) in this study.

Table 1 – One Month EDX Examination

Fiber Sample & Glass Type	Known E-Glass Composition	1 E-Glass	2 E-Glass	3 E-Glass	4 E-Glass	5 E-Glass	6 Advantex® glass	7 Advantex® glass	8 Advantex® glass	9 Advantex® glass	Known Advantex® glass composition
Oxides	%	%	%	%	%	%	%	%	%	%	%
SiO ₂	55.3	61	92	61	74	99	61	62	62	62	59.9
Al ₂ O ₃	14.2	15	4.3	15	9.6		12	12	12	13	13.3
CaO	22.9	24	3.9	23	16		23	23	23	21	22.3
MgO	0.5			0.6			2.8	2.6	2.7	2.8	2.9
B ₂ O ₃	5.8										
Na ₂ O + K ₂ O	0.6	0.9		1	0.8		0.7	0.8	0.8	0.5	0.8
TiO ₂	<.1					0.6					0.4
Fe ₂ O ₃	0.4										0.3
F ₂	0.3										
SrO	0.1										<.1

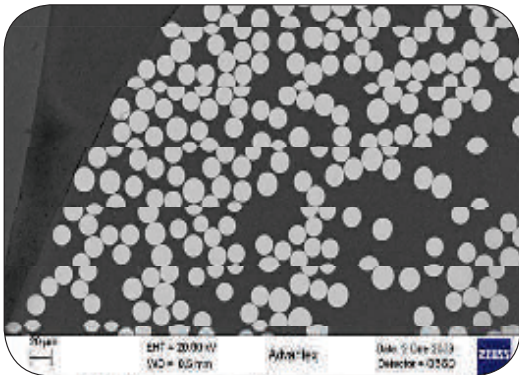


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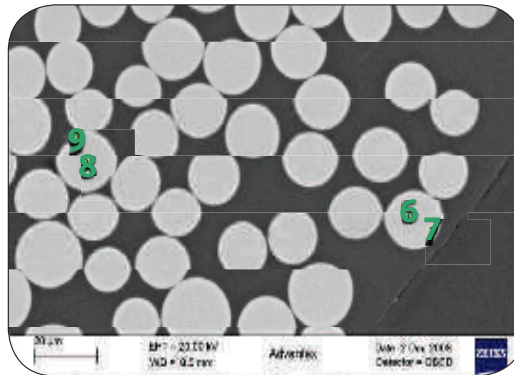
Despite the limitations of EDX, it can be seen that the difference between non-corroded fibers 1 and 3 and corroded fibers 2, 4, and 5 are huge (see green numbering of fibers in photos 4 and 5 on page 5). The increase in silica content in 2, 4, and 5 and the disappearance of boron (earlier work) and reduction in alumina and calcium are indications that most of the glass components (except silica) are being leached from the fibers. This is after a relatively short period of exposure to 10% sulfuric acid under no stress.

“Deformation of the rod has occurred as the E-glass deteriorates.”

Conversely, photos 6 and 7 show no gray (corroded) sections of fibers and Table 1 shows little if any change in the Advantex® glass composition, regardless of the sampling location. Since Advantex® glass does not contain boron, EDX provides a true analysis of the glass composition.



6. Advantex® glass rod, one month 10% H₂SO₄



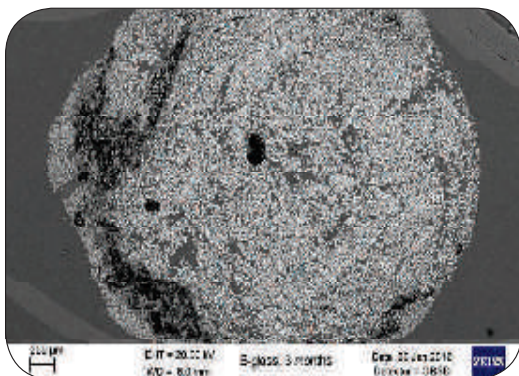
7. Advantex® glass rod, one month 10% H₂SO₄

Exposure Extended

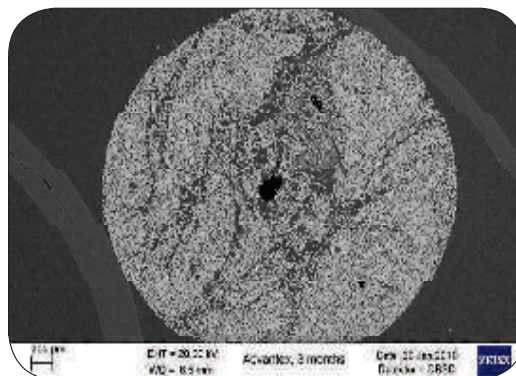
While the resistance to corrosion of the Advantex® glass compared to E-glass at one month is dramatic, it was decided to continue the work to see if any new information could be gleaned from longer exposure times. Photos 8 through 13 show E-glass and Advantex® glass composite rods after three-month exposure in 10% sulfuric acid.

The E-glass sample shows gray fibers along the entire perimeter of the rod and considerable damage on the left-hand side of the photo. Deformation of the rod has occurred as the E-glass deteriorates. Photos 10 and 11 show a higher magnification of this area and the de-bonding and subsequent fracturing that occurs. Little if any deterioration of the resin has occurred although some resin and glass shards likely have been washed away in the polishing and washing of the sample during preparation.

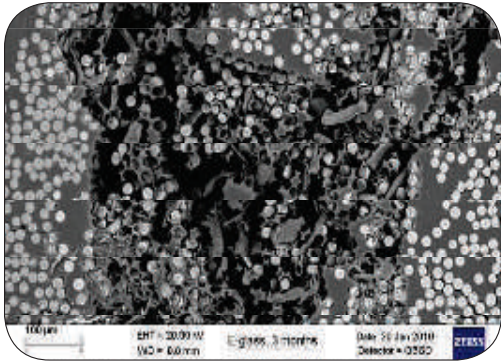
In the examination of the samples, no resin deterioration was apparent. In all of the locations where E-glass fiber was initially present, the resin shows clear patterns from the glass with crisp edges on the resin shards.



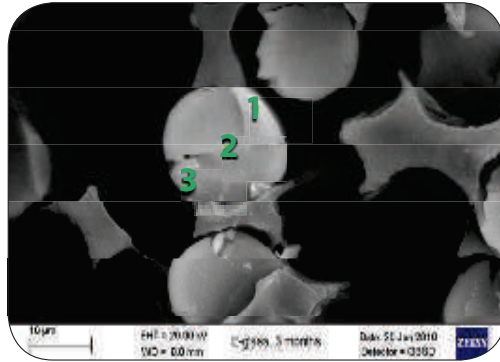
8. E-glass rod, three months 10% H₂SO₄



9. Advantex® rod, three months 10% H₂SO₄

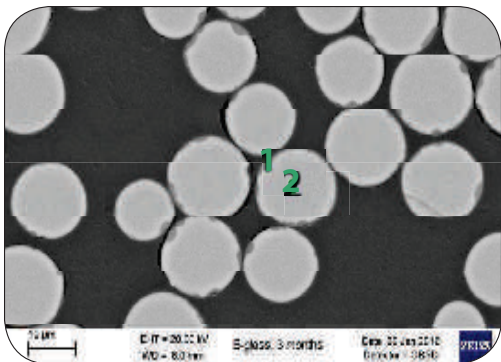


10. E-glass rod, three months 10% H₂SO₄

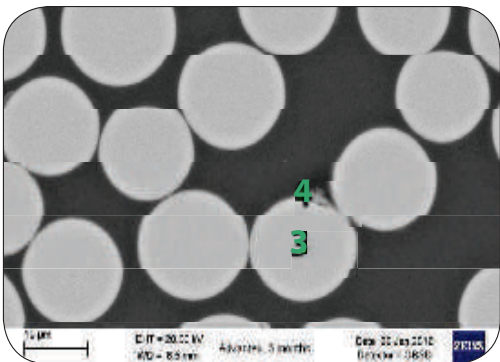


11. E-glass rod, three months 10% H₂SO₄

Photos 12 and 13 show EDX samples of selected areas along the corroded rods. The results are displayed in Table 2. The results for the E-glass sample were not unexpected and are similar to previous EDX sampling at one month. However, the gray area in photo 13 was completely unexpected because Advantex® glass was not expected to corrode. EDX analysis showed that the composition of sections 3 and 4 were nearly identical and showed no corrosion. Closer examination of the gray area in photo 13 showed it to be a chip on the filament which scatters light differently.



12. E-glass rod, three months 10% H₂SO₄



13. Advantex® rod, three months 10% H₂SO₄

Another seemingly puzzling feature of both E-glass and Advantex® glass photos are the large patches of gray. Corroded fibers are not unusual for E-glass rods but were unexpected for Advantex® rods. Photo 9 shows a hint of the problem, but curiously, all the fibers look non-corroded. A closer examination (see photos 14 and 15) of the Advantex® glass-reinforced rod shows that these are not corroded fibers. Instead, a crystalline deposit has formed on the cross-section of the rods scattering the light to make the surface look gray under low magnification.

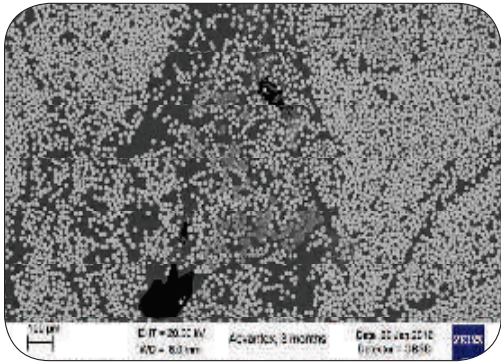
An EDX analysis of the sample area in photo 15 (green star) is shown in Table 2. The analysis shows C (carbon), O (oxygen) and S (sulfur). Although there is enough oxygen to suggest this could be a mixture of carbonates and sulfates, it seems odd the carbonates could exist in this previously acidic environment.

No conclusion as to the nature of these crystals has been made. No cations were found in the vicinity of the crystals which might have indicated a leaching of components from the glass. A survey of both the E-glass and Advantex® rods show that these crystals appear more prevalent in the vicinity of cracks and voids. Additionally, it should be remembered that EDX cannot detect atomic numbers lower than Carbon. The only likely candidates having atomic numbers lower than carbon are boron and hydrogen. However, Advantex® does not contain boron.

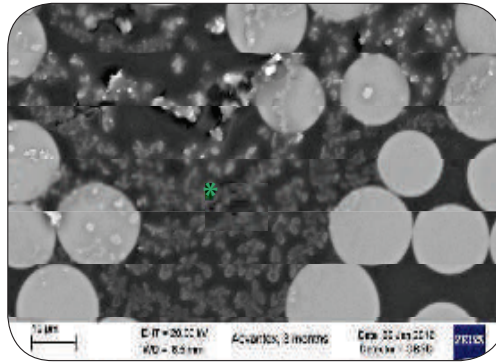


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Since the preparation of a sample for SEM requires putting the samples under very low pressure (vacuum) for an extended period of time, it is suspected that these might be sulfuric acid crystals. But then a higher level of sulfur in the analysis would be suspected. Sulfur is present and it begs the question of how the acid (or sulfate compound) could have migrated through a seemingly intact rod. Either diffusion is occurring through the resin matrix or cracks formed in the resin matrix as a result of previously straining the rods prior to immersion. In any event, this mystery appears to be a fertile area for investigation.



14. Advantex® glass rod, three months 10% H₂SO₄



15. Advantex® glass rod, three months 10% H₂SO₄

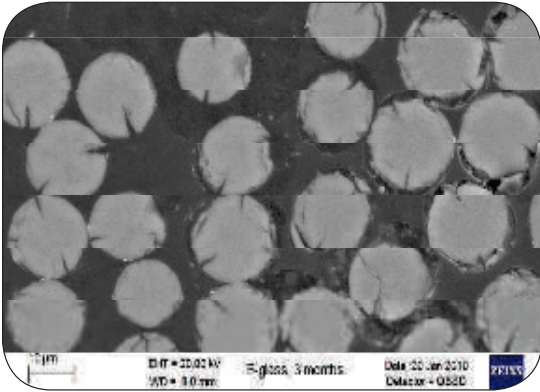
Table 2 – Three Month EDX Examination

Fiber Sample	0	1	2	3	4	*	Advantex® Glass (known composition)
Glass type	E (known composition)	E	E	Adv	Adv	Adv	
Oxides	%	%	%	%	%	%	%
SiO ₂	55.3	83	61	61	60	0	59.9
Al ₂ O ₃	14.2	7	14	13	12	0	13.3
CaO	22.9	10	23	23	24	0	22.3
MgO	0.5		0.5	2.6	3	0	2.9
B ₂ O ₃	5.8						
Na ₂ O + K ₂ O	0.6		1.2	0.6	0.7	0	0.8
TiO ₂	<.1						0.4
Fe ₂ O ₃	0.4						0.3
F ₂	0.3						
SrO	0.1						<.1
S						2	
C						26	
O						72	

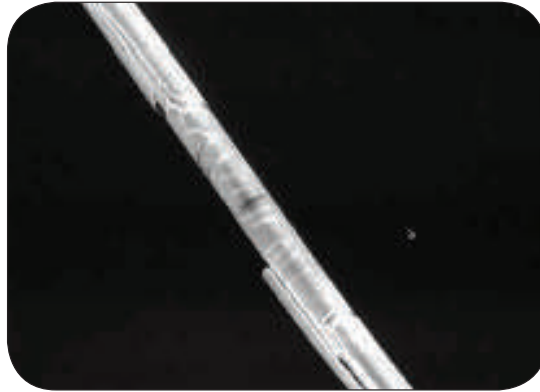


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Lastly, another series of interesting pictures confirms observations seen earlier and presented in the literature³. Both photos 16 and 17 are of E-glass fibers. Photo 16 was taken in the same series of pictures as photos 1 through 15 and is a very high magnification of E-glass fiber composites rods exposed to 10% sulfuric acid for three months. The end view of these fibers shows cracks very similar to helical cracks that typically form on E-glass exposed to corrosive environments. Photo 17, taken several years earlier of the exact same package of E-glass, shows a single filament of E-glass exposed to 5% hydrochloric acid for two hours at 96°C under no load.



16. E-glass rod, three months 10% H₂SO₄



17. E-glass fiber 2 hrs @96C in 5% HCl

Conclusion

Boron-free Advantex® E-CR glass fibers demonstrate superior corrosion resistance compared to E-glass when used as reinforcement in composite structures exposed to sulfuric acid. Previous work on the leaching mechanism of E-glass in strong acids has also been confirmed. Although the technique leaves a number of unanswered questions in this study, it appears that coupling SEM with EDX can answer a number of questions about the corrosion mechanism not easily answered by other techniques.

“**Boron-free Advantex® E-CR glass fibers demonstrate superior corrosion resistance compared to E-glass when used as reinforcement in composite structures exposed to sulfuric acid.**”



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Acknowledgements

Thanks to Roger Shaw for preparing the rods.

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